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(54) Removal of CO₂ from Gas Mixtures

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REMOVAL OF CO₂ FROM GAS MIXTURES

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ABSTRACT

An improved, catalyzed process for the removal of CO₂ from gas mixtures is described using a solution containing 15-40% by weight of potassium carbonate in which the absorption efficiency is enhanced by the addition of sodium or potassium vanadate equivalent to 2 to 10% by weight of V₂O₅ and sodium or potassium borate equivalent to 1 to 10% by weight of KBO₂ in which the weight ratio of equivalent KBO₂ to equivalent V₂O₅ is less than 1.5:1. It has been found that use of the described catalysts permits significant reductions in solution circulation rates (up to 45%), which leads to equipment and utility economies.

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35 (Docket No. 17826)


REMOVAL OF CO₂ FROM GAS MIXTURES

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5 This invention relates to a process for the removal of CO₂ from gas mixtures by means of aqueous solutions of potassium carbonate containing potassium vanadate and borate additives in a defined ratio and with concomitant reductions in scrubbing solution flow rates.

10 The removal of CO₂ from gas mixtures with aqueous potassium carbonate solutions is well known. The absorption is generally done with a hot solution as described in U. S. Patent No. 2,886,405. The efficiency of the process is
15 greatly enhanced by the use of amine and especially by amine borate additives described in U. S. Patents Nos. 4,271,132 and 3,851,041 of A. G. Eickmeyer.

20 However, such organic additives are subject to oxidative degradation when scrubbing gases containing oxygen, especially at elevated temperatures. This causes the solution to lose absorption efficiency and to accumulate undesirable oxidation products. For the same reasons
25 such solutions cannot be regenerated by means of air stripping.

30 In addition, the equipment and utility costs associated with CO₂ removal plants are considerable; therefore, workers in the art are continuously searching for ways to lower such costs. One possibility is to lower the circulation rate of the scrubbing solution, which saves money on equipment (e.g., smaller pumps and towers) and also on steam in the regeneration section.
35 Obviously, however, such cost saving mea-



1 sures can be effected only if the scrubbing solution, at design concentrations and temperatures, is capable of handling the gas removal load at the lowered circulation rates.

5 Gas mixtures for which the present invention is well suited include recycle gas in the production of ethylene oxide from ethylene and oxygen, flue gas and lime kiln gas.

10 U. S. Patent No. 3,907,969 of Joseph H. Field discloses aqueous solutions of potassium carbonate containing KBO_2 and V_2O_5 in which the weight ratio of equivalent KBO_2 to equivalent V_2O_5 is at least 1.5:1. The tests described in this patent indicate that the CO_2 absorption rate is improved by the addition of both KBO_2 and V_2O_5 but that the CO_2 pickup of the solution is increased by the KBO_2 and decreased by the V_2O_5 . Therefore the weight ratio of KBO_2 to V_2O_5 is specified to be at least 1.5:1. Indeed, in Table IV of this patent results are set forth which demonstrate that, at $\text{KBO}_2/\text{V}_2\text{O}_5$ ratios of less than 1.5:1 CO_2 pickup is decreased as compared with the control.

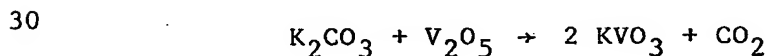
15 Surprisingly, it has been discovered that both the absorption rate and the CO_2 pickup are increased by increasing additions of V_2O_5 to potassium carbonate solution and that it is actually preferable to have a weight ratio of KBO_2 to V_2O_5 of less than 1.5:1. Further, the systems of the invention can be advantageously operated at circulation rates significantly below the rates employed with a comparable (i.e., the same K_2CO_3 concentration and temperature) non-catalyzed hot potassium carbonate solution, when scrubbing identical gas streams. Such reduction can be up to 45%, and preferably from about 30 to 40%.

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1 The scrubbing solutions hereof use K_2CO_3
as the principal salt in concentrations from 15%
to 40% by weight and preferably from 20% to 30% by
weight. The solutions are usually cycled between
5 an absorption stage, where CO_2 is picked up by the
solution from the gas, and a regeneration stage,
where CO_2 is desorbed from the solution by steam
or air stripping. The absorption is preferably
conducted at superatmospheric pressure and the
10 regeneration is preferably at near atmospheric
pressure. The absorption temperature may be
substantially the same as the regeneration tem-
perature. In some cases a small amount of cooled
solution may be sent to the top of the absorber in
order to remove CO_2 down to a low level.

15 Some CO_2 remains dissolved even in the
regenerated solution, where it is present at
 $KHCO_3$. Thus a regenerated solution of 25% equiva-
lent K_2CO_3 with 30% of the K_2CO_3 converted to
20 $KHCO_3$ would have 17.5% K_2CO_3 and 10.85% $KHCO_3$ by
weight.

 Sodium or potassium vanadate is added to
the solutions in an amount from 2% to 10% by
weight of equivalent V_2O_5 . The preferred concen-
25 tration is from 3% to 8% by weight equivalent
 V_2O_5 . The vanadate may be added as the sodium,
potassium or ammonium meta vanadate or it may be
formed in place by dissolving V_2O_5 in the K_2CO_3
solution as follows:

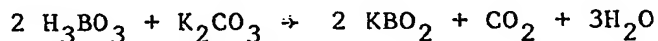


 Also it may be added as sodium or potassium pyro-
vanadate, $Na_4V_2O_7$ or $K_4V_2O_7$, or it may be pre-
35 formed by reacting V_2O_5 with KOH solution.

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1 Taking into account the equivalent weights, the addition of 1.52% by weight of KVO_3 or 1.34% NaVO_3 gives 1% by weight of equivalent V_2O_5 .

5 The effective amount of sodium or potassium borate in the scrubbing solutions of the invention is in the range of from 1% to 10% by weight of equivalent KBO_2 and the preferred range is from 2% to 8% by weight of equivalent KBO_2 .
10 The borate may be added as sodium or potassium metaborate, $\text{Na}_2\text{B}_2\text{O}_4$ or $\text{K}_2\text{B}_2\text{O}_4$, or sodium or potassium tetraborate, $\text{Na}_2\text{B}_4\text{O}_7$, or $\text{K}_2\text{B}_4\text{O}_7 \cdot 8\text{H}_2\text{O}$, or as other borate salts. Also it can be formed by adding boric acid to potassium carbonate solution as follows:



15 In this case the addition of 0.755% by weight of H_3BO_3 gives 1% by weight of equivalent KBO_2 .

20 In typical systems of the invention, the temperature of the absorption solution is maintained within the range of 180-250° F; typical pressures within the absorption stage range from 200-500 psig.

EXAMPLES

25 The relative rates of CO_2 absorption and the relative pickup of CO_2 was measured at 80° C. using 25% by weight of aqueous K_2CO_3 solution without and with various amounts of V_2O_5 and boric acid added to give the specified percentages of V_2O_5 and equivalent KBO_2 shown on Table I. Percentage reductions in circulation rate when using
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1 the compositions of the invention as compared with
a non-catalyzed control were also determined.

5 TABLE I

Run	K_2CO_3	V_2O_5	KBO_2	RATE	CO_2 PICKUP	CALCULATED PERCENTAGE REDUCTION IN CIRCULATION RATE
A	25	0	0	1.00	1.00	--
10 B	25	2	4	2.91	1.45	31%
C	25	4	2	3.79	1.54	35%
D	25	8	2	6.21	1.71	42.5%
E	25	8	8	5.21	1.63	38.7%

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25 The relative rate of CO_2 absorption was
determined by comparing the pseudo first order
absorption rate, that is the natural logarithm of
the ratio of the CO_2 entering to the CO_2 leaving,
for solutions having the same equilibrium back
pressure. The increased CO_2 pickup of the more
active solutions is believed to result from better
regeneration of the lean solution and a closer
30 approach to equilibrium for the rich solution,
thus giving a higher solution conversion range or
"pickup."

35 Comparing runs B and C shows that a 2:1
ratio of V_2O_5 to KBO_2 (run C) rather than a 2:1
ratio of KBO_2 to V_2O_5 (run B) gives an appreciable

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1 increase in the relative absorption rate as well as
the CO₂ pickup. Comparing runs C and D shows that
doubling the V₂O₅ content, while holding the KBO₂
the same, enhances the solution effectiveness
5 appreciably. Comparison of runs D and E shows
that increasing the KBO₂ with the same V₂O₅ de-
creases the solution effectiveness somewhat.
Also, as set forth in the righthand column, the
solutions permit very significant reductions in
10 circulation rates and therefore give the attendant
advantages noted above.

Since the solutions hereof are not
subject to oxidative degradation they are well
suited to removal of CO₂ from gases also contain-
15 ing oxygen, such as ethylene oxide recycle gas,
flue gas and lime kiln gas. For the same reason
it is practical to regenerate the solutions by
means of air stripping or a combination of air and
steam stripping.

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1 Claims

1. In a method for absorbing CO_2 from a gas mixture containing the same wherein a hot absorption solution having from 15 to 40% by weight of potassium carbonate is continuously circulated at a circulation rate through an absorption stage and a regeneration stage, said gas mixture is contacted with said solution in said absorption stage to absorb CO_2 from the mixture, and said solution is thereafter regenerated in said regeneration stage by removal of CO_2 therefrom, the improvement which comprises the steps of:

adding to said solution from about 2 to 10% by weight equivalent V_2O_5 and from about 1 to 10% by weight of equivalent KBO_2 , the weight ratio of equivalent KBO_2 to equivalent V_2O_5 being less than 1.5:1; and reducing said circulation rate by an amount of up to about 45%.

2. The method of Claim 1, said circulation rate being reduced by an amount of about 30 to 40%.

3. The method of Claim 1 wherein the concentration of equivalent V_2O_5 is from about 3 to 8% by weight, and the concentration of equivalent KBO_2 is from about 2 to 8% by weight.

4. The method of Claim 1 wherein the weight ratio of equivalent KBO_2 to equivalent V_2O_5 is less than 1:1.

1 5. The method of Claim 1 wherein the
concentration of potassium carbonate in said solution
is from about 20 to 30% by weight.

5 6. The method of Claim 1, said absorp-
tion being carried out at superatmospheric pressures.

7. The method of Claim 1, said regenera-
tion including the steps of steam stripping said
10 solution.

8. The method of Claim 1, the tempera-
ture of said solution during said absorption step
being approximately the same as the temperature
15 thereof during said regeneration step.

9. The method of Claim 1, said solution
being at a temperature of from about 180 to 250° F.

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